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THE AMMONATION OF
CIS-DICHLORODIAMMINEPALLADIUM(II)

James Richards Atwill

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THESIS

THE AMMONATION OF
cis-DICHLORODIAMMINEPALLADIUM(II)

by

James Richards Atwill, Jr.

Thesis Advisor:

R. A. Reinhardt

June 1973

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The Ammonation of
cis-Dichlorodiamminepalladium(II)

by

James Richards Atwill, Jr.
Lieutenant, United States Navy
B.S., Georgia Institute of Technology, 1967

Submitted in partial fulfillment of the
requirements for the degree of

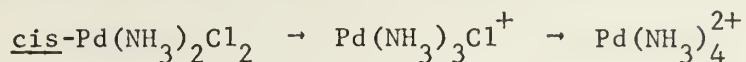
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NAVAL POSTGRADUATE SCHOOL
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ABSTRACT

The reaction of cis-dichlorodiamminepalladium(II) with ammonia:



was studied over the temperature range 10°-21°C using ultraviolet spectroscopy. Three chloride concentrations were utilized in the kinetic runs; 0.50M, 0.40M, and 0.05M, and in all runs $\mu = 1.0\text{M}$.

Slow and fast steps are identified and the observed rate constants for these steps, k'_s and k'_f respectively, were obtained. The following extrapolated values were calculated for 25°C: $k'_s = 32.5 \text{ sec}^{-1}$, and $k'_f = 310 \text{ sec}^{-1}$. Using these values, comparisons are drawn with previously reported data.

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I. INTRODUCTION

A. GENERAL

As one of the elements in the nickel family, palladium in its plus-two oxidation state characteristically forms square-planar complexes. This geometry is particularly favorable for substitution by an associative mechanism since there are two coordination positions open for attack by an entering group. The transition state intermediate for these substitutions in palladium(II) and the square planar d^8 systems is thought to involve a trigonal bipyramidal structure (Ref. 1).

Kinetic studies of substitution reactions in square planar complexes have shown that the following two term rate law generally obtains:

$$-d(\text{complex})/dt = [k_1 + k_2(Y)](\text{complex})$$

where k_1 and k_2 are first- and second-order rate constants respectively and (Y) is the concentration of the entering ligand.

The second-order term is consistent with direct attack by Y upon the substrate. A mechanism consistent with the first order term is one in which the leaving group X is replaced by a solvent molecule, which is in turn rapidly replaced by the entering group. The rate law then assumes the following form:

$$-d(\text{complex})/dt = [k_s(S) + k_2(Y)](\text{complex})$$

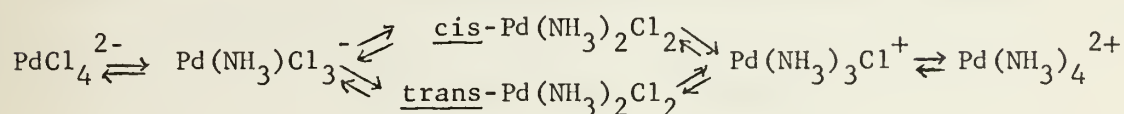
where $k_s(S) = k_1$. If, on the other hand, the rate determining step in this reaction pathway is the replacement of the solvent molecule by the entering group, the rate becomes:

$$-d(\text{complex})/dt = [k_1(Y)/(X) + k_2(Y)](\text{complex})$$

The latter form was found by Monk (Ref. 2) to apply to the reaction of ammonia with PdCl_4^{2-} and with cis- $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$.

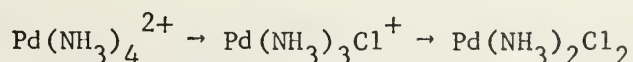
B. cis-DIAMMINEDICHLOROPALLADIUM(II)

In previous works (Ref. 2-9) a number of authors have dealt with the problem of identifying the various rate constants and equilibrium constants involved in the following reaction sequence for the chloroammine complexes of palladium(II):



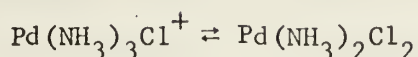
It was the intent of the present investigation to deal more specifically with the reaction of cis- $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ and ammonia to give, consecutively, $\text{Pd}(\text{NH}_3)_3\text{Cl}^+$ and $\text{Pd}(\text{NH}_3)_4^{2+}$. Although there have been previous investigations that studied this particular reaction, or portions of it, the understanding of this reaction sequence was by no means complete. Additionally, there was the problem of verifying the results already reported, since, for reasons elaborated upon below, most of the previous data were obtained with a moderate degree of uncertainty. Table V summarizes the results of previous investigations that were germane to this research effort.

Reinhardt and Sparkes, in Ref. 4, assumed that the reaction of chloride with tetraamminepalladium(II),

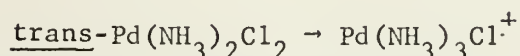


led largely to the formation of the trans isomer of diamminedichloro-

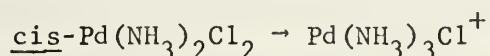
palladium(II) and evaluated the rate constants accordingly. In Ref 3 the equilibrium constant for



was evaluated. These values, with the assumption cited above, then made possible the calculation of the rate constant for the reverse step, namely:



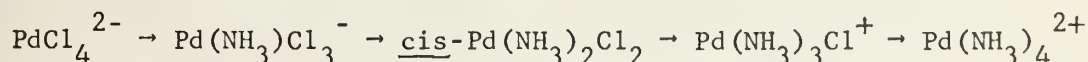
since $K_{\text{eq}} = k_{\text{fwd}}/k_{\text{rev}}$. By evaluating the rate constant for the reaction



and comparing it with that calculated above, for what was assumed to be the trans isomer, this author hoped to determine if Reinhardt and Sparkes had been correct in their assumption.

Midas, (Ref. 7) on the other hand, specifically studied the reaction of the cis isomer with ammonia. Interpretation of his results, however, was clouded by two factors. First, the use of an ionic strength of 0.8M made comparison with studies at unit ionic strength difficult. Secondly, the low ammonia concentration used, approximately 10^{-5}M , meant that reversibility in the reaction sequence was appreciable, thus enormously complicating the rigorous interpretation of the kinetics.

Reinhardt and Monk (Ref. 6) studied the kinetics of the following reaction sequence:

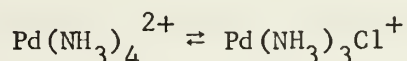


These were experiments carried out in 10 cm cells using rather slow mixing rates. Only two of the four possible steps shown above could be



observed in the time scale of the measurements. It was assumed that the remaining steps were too fast to be seen and, on the basis of a rather involved series of arguments, that the faster of the observed steps was the first and the slower, the third, (cis-Pd(NH₃)₂Cl₂ → Pd(NH₃)₃Cl⁺). In addition, these experiments were carried out at the low ammonia concentration used by Midas and thus the results are also subject to the uncertainties resulting from reversibility discussed above in connection with that work.

To avoid the limitations of those aforementioned studies, the present author sought to utilize a concentration of ammonia sufficient to insure minimal interference from reversible steps in the reaction sequence. Using the equilibrium constant (Ref. 3) for the reaction



and the reactant concentrations utilized by this author, a simple calculation showed that the reaction of cis-diamminedichloropalladium(II) with ammonia proceeded at least 86% to the final product Pd(NH₃)₄²⁺. At such ammonia concentrations, however, the reaction rate is so great that it was necessary to make use of a more rapid mixing technique than had been employed earlier. The injection by hypodermic needle of one solution into another was found to give essentially complete mixing in less than three seconds (as shown by consistency of kinetic results) when carried out in 1 cm cells. In order to work at sufficiently low concentrations it was thus decided to measure absorbance in the charge transfer region of the ultraviolet. At wavelengths in the range 232-235 nm, a 1.00 x 10⁻⁴ formal solution of cis-Pd(NH₃)₂Cl₂ in 1.0 M sodium chloride was found to have an absorbance of approximately 0.9-0.7; thus this wavelength range was considered a good choice for studying

the reaction.

It was felt that to obtain meaningful data from the DK-1A recording spectrophotometer, a reaction halftime of at least ten seconds would be needed. To meet this time requirement, a solution of $1.0 \times 10^{-3} \text{ M}$ ammonia in 1.0 M ammonium perchlorate was about the maximum concentration of ammonia that could be utilized in the equal volume mixing scheme to be employed in the study. This meant that the reaction mixture would be 5×10^{-5} formal in palladium complex and $5 \times 10^{-4} \text{ M}$ in ammonia. Although a ratio of ammonia to complex of 100:1 would have been ideal for the kinetic interpretation, for reasons detailed later (see Treatment of Data and Results), the 10:1 ratio was certainly satisfactory. Additionally, this $5 \times 10^{-4} \text{ M}$ ammonia concentration in the reaction mixture was a 50-fold increase over that used in previous research (Refs. 6, 7).



II. EXPERIMENTAL

A. MATERIALS

All materials in this research, except the palladium complexes, were reagent grade and were used without further purification. Trans-dichloro-diamminepalladium(II) was obtained from Alfa Inorganics, lot number Pd-14. Cis-diamminedichloropalladium(II) was prepared from tetraamminepalladium(II) perchlorate solution using the method of Coe and Lyons (Ref. 10), modified as below:

1. Preparation of Tetraamminepalladium(II) Chloride Monohydrate

Initially this preparation was attempted following the method used by DeBerry (Ref. 11) in which trans- $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ was dissolved in concentrated aqueous ammonia and left to evaporate to dryness. Although the characteristic colorless needles of $\text{Pd}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$ were formed in this process, the product was invariably contaminated with a yellow crystalline material. By comparison of IR spectra it was concluded that the contaminant was not starting materia; however, no further characterization was attempted.

An alternate preparation was then tried utilizing liquid ammonia as the solvent. This method yielded the desired product far more rapidly than the previous synthesis and without the obvious impurities.

2. Preparation of Aqueous Tetraamminepalladium(II) Perchlorate Solutions

Dissolving 1.7g of the $\text{Pd}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$ prepared above in 25 ml of water gave a solution rich in chloride. To prepare successfully the cis- $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ the chloride had to be totally removed and replaced with perchlorate. This was accomplished by the addition of an equivalent



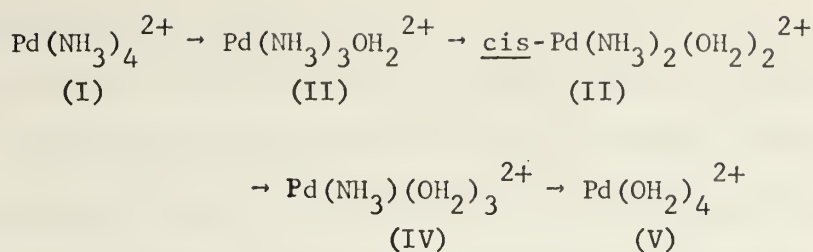
amount of silver perchlorate, thus precipitating silver chloride. Since an excess of either silver ion or chloride ion would have been detrimental to the ultimate preparation of the cis isomer, the addition of silver perchlorate was necessarily stoichiometric. A solution approximately 0.2 M in silver perchlorate was made up and titrated against four 0.10 ml aliquots using the Fajan's method (Ref. 12). Each aliquot was weighed and then diluted with ten ml of water before titration. The amount of silver perchlorate required for the remaining tetraamminepalladium(II) chloride solution was calculated and added. The solution was filtered to remove the solid silver chloride and then a portion was tested for residual chloride by the addition of a drop of silver perchlorate. This procedure was repeated until the test for chloride was negative and the addition of a drop of dilute sodium chloride to a second sample of the solution showed no excess silver ion to be present as well.

3. Preparation of cis-Diamminedichloropalladium(II)

The solution of $\text{Pd}(\text{NH}_3)_4(\text{ClO}_4)_2$ made up above was divided into two portions, each containing about 1.2g of tetraamminepalladium(II) perchlorate. To the first portion, 1.3g of 60% perchloric acid were added and it was allowed to stand. After 16 hours, concentrated sodium chloride solution was added and the yellow-orange crystals of cis- $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ were collected.

From studies of the reaction rates involved, (Ref 11) Reinhardt¹ suggested that the second portion be allowed to stand only four hours before the addition of sodium chloride in order to improve the yield. Since the reaction sequence initiated by the addition of perchloric acid was:

¹ See Reference 13.



the addition of chloride in the presence of I or II would have precipitated the trans-Pd(NH₃)₂Cl₂ isomer, thus contaminating the product. Species III in the presence of chloride would have given the desired product; whereas both IV and V would have led, in time, to the production of PdCl₄²⁻, which would remain in solution.

By allowing the second portion of the preparation to stand only four hours, the concentrations of I and II became negligible without providing enough time for the concentrations of IV and V to become excessive. The yield realized from the second portion was, in fact, the larger of the two and subsequent analysis also indicated that it was the purer.

B. ANALYSIS OF cis-DIAMMINEDICHLOROPALLADIUM(II)

1. Infrared Analysis

The infrared spectrum of the product as a Nujol mull failed to show the Pd-N stretching vibrations at 484 and 463 cm⁻¹ characteristic of cis-Pd(NH₃)₂Cl₂ which Midas reported in Ref. 7 and Durig et al in Ref. 14. Spectra of the product in KBr disc form kindly taken by Mr. J. L. Bernard of the Perkin Elmer Corporation on a model 467 IR spectrophotometer clearly showed these characteristic peaks and closely reproduced the spectrum obtained by Midas. Based on a comparison of these spectra with those of Midas, it was concluded that the product from the second portion of the preparation was the purer of the two.

2. Potassium Iodide-Acetone Test

In this test, a small amount of product added to a test tube containing a colorless solution of KI in acetone rapidly produced a red color as the tube was shaken, a positive test for the cis-Pd(NH₃)₂Cl₂ isomer (Ref. 15). A control sample of the stock trans isomer was added to a second test tube, but no significant color change could be observed after five minutes of shaking. In fact, nearly two hours passed before the trans-complex reached the same dark red coloration. Samples from both portions of the product gave identical results in the test so no distinction in purity could be inferred.

3. Conclusion

From the results of the above checks it was concluded that the products of both portions of the synthesis were cis-Pd(NH₃)₂Cl₂ of adequate purity.

C. EQUIPMENT

IR spectra were taken on a Perkin-Elmer 621 grating spectrophotometer. Spectral scans and kinetic runs were made on a Beckman model DK-1A recording spectrophotometer using one-cm silica cells. Thermostatic control was maintained by utilizing a Beckman thermostated cell holder connected to a Forma temperature bath and circulator. This same bath was simultaneously used to store the solutions for the kinetic runs at the temperatures desired. Accurate determination of the temperature of the sample solutions during reactions was accomplished by attaching a copper-constantan type T thermocouple, enclosed in a capillary tube, to the interior of the sample cell. The thermocouple used an ice bath cold junction and was monitored by a Honeywell Electronik 19 recorder. Data were analyzed using a Hewlett Packard model 9810 calculator.

D. KINETIC RUNS

The reactions of cis-Pd(NH₃)₂Cl₂ with NH₃ were observed by following the change in absorbance with time in the uv wavelength region, usually at a wavelength of 235 nm. All reactions were run at an ionic strength of 1.0. In each reaction, equal volumes of palladium complex and initiating solution were mixed. The cis isomer was made up to be 1.00×10^{-4} formal in solutions that were 1.0, 0.80, and 0.10 M in sodium chloride. These solutions were made up by dissolving 0.0106 g of complex in 50 ml of the NaCl solvent and then taking a ten-ml aliquot and diluting it to 100 ml. This particular scheme was chosen to minimize errors in measurements while avoiding unnecessarily large volumes of solution. When sodium chloride concentrations were to be less than 1.0 M, the ionic strength was maintained at 1.0 by the addition of sodium perchlorate. All solutions of cis-Pd(NH₃)₂Cl₂ were used within 24 hours of the time that they were made up.

Initiating solutions for the reaction were designed to be approximately 1.0×10^{-3} M in ammonia and 1.0 M in ammonium perchlorate. The exact ammonia concentration was determined by titration with a standard hydrochloric acid solution using a mixed indicator containing bromcresol green and methyl red in roughly equal proportions. Both sample and initiating solutions were made using boiled distilled water and were stored under a nitrogen atmosphere to insure the absence of carbon dioxide.

Final reaction mixtures, then, contained palladium complex at a concentration of 5.0×10^{-5} formal in solutions which were 0.50, 0.40, and 0.05 M in NaCl and 5×10^{-4} M in ammonia. For each of the three chloride concentrations involved, individual kinetic runs were made at various temperatures in the range 10°C - 20°C with an occasional run at

a temperature of about 21°C.

Prior to each kinetic run, the sample cell was rinsed six times with distilled water, three times with sample solution, and allowed to drain. Next the sample cell was loaded by pipetting in 1.5 ml of sample solution from a graduated pipette. The loaded cell was then placed into the thermostated cell holder and left until the thermocouple indicated that the solution had reached the ambient temperature. This usually required from one to ten minutes. At that point a graduated hypodermic syringe, which was kept chilled in a refrigerator for lower temperature runs, was used to inject rapidly 1.5 ml of initiating solution into the sample cell. From the internal agreement shown by data points at times of $t_0 + 3$ seconds and beyond, it was concluded that complete mixing was obtained in less than three seconds. A continuous recording of the temperature of the reaction mixture was obtained.

The graduated pipette used to load the sample cell and the syringe used to inject the initiating solution were calibrated by weighing out samples of distilled water and were found to be reliable to within one percent in the amount of water delivered.

In spite of being enclosed in a glass capillary tube, the thermocouple wires responded consistently to temperature changes in the cell in less than one second. The temperature for a given kinetic run was determined by averaging the recorded reaction temperature in the time range $t_0 + 5$ seconds through $t_0 + 70$ seconds for the slower runs and in the range $t_0 + 5$ seconds through $t_0 + 40$ seconds for the more rapid ones. The temperature was assigned to the nearest 0.1°C and it was felt that in all runs this assignment was accurate to within $\pm 0.1^\circ\text{C}$.

The absorbance vs. time traces on the DK-1A spectrophotometer were recorded using a chart speed of 15 cm/min which yielded a 4 sec/cm time

scale on the trace. Absorbance readings could easily be obtained for every second of elapsed time; however, this was done only on the rapid runs in order to obtain a sufficient number of data points. Two- and four-second intervals were used for the slower runs. The start time for the reaction, too, was clearly marked by an instantaneous change on the absorbance trace. For runs in which 0.10 M sodium chloride solutions of complex were mixed with the ammonia-ammonium perchlorate solution, this change appeared only as a drop in absorbance. On the other hand, when the complex was dissolved in 0.80 or 1.0 M sodium chloride, the mixing process produced a sharp upward spike in absorbance followed by the typical decay pattern. The latter behavior was almost certainly the result of refractive index differences between the two solutions concerned. D_{∞} values were normally reached in five to ten minutes of elapsed time, depending upon the reaction conditions.

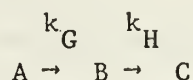
Data for the slower runs were taken out to 75 sec elapsed time and for the more rapid runs, out to about 40 sec. In either case this covered a range of about two to three half-times of the reaction.



III. TREATMENT OF DATA AND RESULTS

A. THE REACTION $\text{cis-Pd(NH}_3)_2\text{Cl}_2 \rightarrow \text{Pd(NH}_3)_4^{2+}$

Under the proper choice of conditions, the above reaction can be made pseudo-first order with respect to the concentration of palladium complex. The reaction then effectively becomes a series first order reaction of the type



as discussed by Frost and Pearson (Ref. 16).

Table I describes the symbology to be used in the remainder of this section. The absorbance for the general reaction shown above, at any time t , can be written

$$D = \left[\epsilon_A(A) + \epsilon_B(B) + \epsilon_C(C) \right] l.$$

Now if ϵ_C is several orders of magnitude smaller than ϵ_A or ϵ_B at the wavelength under consideration,

$$D \approx \left[\epsilon_A(A) + \epsilon_B(B) \right] l.$$

Using the instantaneous values for the concentrations of A and B desired in Ref 16:

$$\begin{aligned} (A) &= (A)_0 e^{-k_G t} \\ (B) &= \frac{(A)_0 k_G}{k_H - k_G} \left(e^{-k_G t} - e^{-k_H t} \right) \end{aligned}$$

the change in absorbance can be expressed by

$$\Delta D = I_A e^{-k_G t} + I_B e^{-k_H t}.$$

When the two pseudo-first order rate constants k_G and k_H are not too nearly equal, they can be evaluated graphically. A plot of $\ln(\Delta D)$ vs. time will be linear at short times with a slope roughly equal to $-k_f$, the faster of the two constants, and will also be linear at long times with a slope of $-k_s$, the slower of the two rate constants. Clearly, the greater the difference between the two constants the more easily they can be determined by this means.

B. PSEUDO-FIRST ORDER KINETICS

For the above strategy to be applicable to a second-order reaction, it is necessary to create pseudo-first order reaction conditions. This is normally accomplished by using a large excess of one reactant so that total consumption of the second reactant makes no appreciable change in the concentration of the first and this concentration can be considered a constant. A ratio of reactant concentrations of 100:1, or greater, would be ideal in this regard, but Corbett (Ref. 17) has shown that valuable results can be obtained with as little as a 2:1 excess. Using a least squares treatment to obtain the pseudo-first order rate constant from plotted synthetic data, Corbett calculated the specific second order rate constant by using the formula

$$k = k'' / (a - m).$$

In this expression, k'' is the observed pseudo-first order rate constant; a , the initial concentration of the reactant in excess; and m , the mean value of the product concentration over the extent of the reaction studied. His calculation, for a case in which the ratio of initial reactant concentrations is 5:1 (the ratio of normalities used in the present study), shows an error of less than 2.5% in the value of k when data are taken out to 80% of complete reaction. For the two to three

half-times of reaction (75% - 88% of completion) over which data were taken in most of the kinetic runs of the present study, a concentration ratio of 5:1 should have allowed determinations of observed rate constants with only about 3% error.

Plots of $\ln(\Delta D)$ vs. time were made for each run. The linear portion of the plot that resulted at long times was back-extrapolated to zero time where the intercept was $\ln(I_s)$ and the slope was $-k_s$, the observed slow step rate constant. This technique is illustrated in the report by Midas (Ref. 7). Then, values for $\Delta D - I_s e^{-k_s t}$ as a function of time were determined and plotted (Ref. 18). Since

$$\Delta D - I_s e^{-k_s t} = I_f e^{-k_f t}$$

a plot of

$$\ln \left[\Delta D - I_s e^{-k_s t} \right]$$

versus time has a slope equal to $-k_f$, the observed fast-step rate constant in this case, and an intercept of $\ln(I_f)$. Next, values of $\Delta D - I_f e^{-k_f t}$ were determined in like fashion. These values where the fast step had been subtracted away were then graphed as before, but now presented a picture of the slow step over the entire time frame of observation. The values of I_s and k_s obtained with the fast step removed in this way were compared with the corresponding values from the extrapolated plot. If the agreement was close, as it was for the majority of the runs, the original value of k_s and the value of k_f were kept. In the cases where the second value of k_s was not in good agreement with the first, a new value of k_f was derived from the second k_s and the whole process was repeated until two successive values of k_s were approximately equal. A least squares program for the Hewlett Packard 9120 computer was used to determine the constants in the few cases where the data points showed

much scatter. In general, though, the internal consistency of the data was such that slopes could easily be determined graphically. As a check on this method, several runs were analyzed by both means and the derived constants were in excellent agreement.

C. EVALUATION OF SPECIFIC RATE CONSTANTS

As detailed above, the method developed by Corbett (Ref. 17) was used to minimize the error in determining the specific rate constants from the pseudo-first order constants. The value of the ammonia concentration $[(a - m) \text{ in Corbett's treatment}]$ which was divided into the observed constant was chosen to be the concentration present when the reaction reached 50% completion, $(\text{NH}_3)_{1/2}$. For example, in a run where the initial ammonia and complex concentrations were $5 \times 10^{-4} \text{ M}$ and $5 \times 10^{-5} \text{ M}$ respectively, this value for $(\text{NH}_3)_{1/2}$ was $4 \times 10^{-4} \text{ M}$.

Because this specific reaction of the cis-isomer with ammonia had been found to obey a two-term rate law (Ref. 2,7) separation of the individual first and second-order specific rate constants (k_1 and k_2) for each step was far more complicated. The observed rate constants had been found to have the following values:

$$k_s = k_{1s} \frac{(\text{NH}_3)}{(\text{Cl}^-)} + k_{2s} (\text{NH}_3)$$

$$k_f = k_{1f} \frac{(\text{NH}_3)}{(\text{Cl}^-)} + k_{2f} (\text{NH}_3)$$

In addition to dividing out the ammonia concentration, it was necessary to have the data from at least two different chloride concentrations in order to separate the component constants. Therefore, the data were obtained from reaction mixtures of 0.50, 0.40, 0.05 M sodium chloride.

Evaluation of k_1 and k_2 for each step (fast and slow), was desired only for the temperatures 10° , 15° , and 20°C . To do this, an Arrhenius plot of $\ln k'$ vs $1/T$ was made for each step at each different chloride concentration used: where

$$k' = \frac{k(\text{Cl}^-)}{(\text{NH}_3)_{1/2}}.$$

For example, in the case of 0.50 M sodium chloride,

$$k'_s = \frac{k_s(\text{Cl}^-)}{(\text{NH}_3)_{1/2}} = k_{1s} + 0.50 k_{2s}$$

and table II is a compilation of the k' values for all of the individual kinetic runs. The points so obtained were fitted by a least squares program to determine the slope and intercept of the plot. The values of k' at each of the three temperatures of interest were taken from this fitted straight line. These "best values" are summarized in Table III along with the activation energies (E_a) discussed below. Figures 1 and 2 illustrate the Arrhenius plots for the 0.50 M chloride solutions. A comparison of k' values for two different chloride concentrations, then, produced a simple system of two simultaneous equations which could be readily solved for k_1 and k_2 . As an illustration, let X equal k'_s for the 0.50 M Cl^- at 10°C and Y equal k'_s for the 0.40 M Cl^- at the same temperature. The resulting equations are:

$$k_{1s} + .5k_{2s} = X$$

$$k_{1s} + .4k_{2s} = Y$$

and the solution is straightforward. Table IV lists the values of the specific rate constants obtained by this method.

TABLE II
SUMMARY OF KINETIC RUNS

$$k' = \frac{k_{\text{obs}}(\text{Cl}^-)}{(\text{NH}_3)_{\frac{1}{2}}} ; \quad (\text{NH}_3)_{\frac{1}{2}} = \text{ammonia concentration when the reaction reaches 50\% completion.}$$

Run No.	$(\text{Cl}^-); (\text{NH}_3)_{\frac{1}{2}}$	$T \pm 0.1^\circ\text{C}$	$k'_s (\text{sec}^{-1})$	$k'_f (\text{sec}^{-1})$
I	a;d	19.7	25.40	272.4
II	a;d	20.6	23.91	258.6
III	a;d	20.6	26.90	243.7
IV	a;d	19.9	23.33	248.3
V	a;d	21.0	29.66	292.0
VI	a;d	21.3	29.31	310.3
VII	a;d	15.7	19.66	204.6
VIII	a;d	16.6	24.25	226.4
IX	a;d	16.0	24.60	252.9
X	a;d	16.2	18.28	180.5
XIV	a;e	10.7	15.76	189.1
XV	a;e	10.6	17.72	190.2
XVI	a;e	10.6	15.98	193.5
XVII	c;e	10.3	5.772	41.52
XVIII	c;e	10.3	6.033	42.83
XIX	c;e	10.3	6.457	43.80
XX	c;e	10.3	6.000	50.00
XXI	c;e	14.6	9.011	76.96
XXII	c;e	14.5	10.54	89.02
XXIII	c;e	14.6	9.587	80.33
XXIV	c;e	14.0	8.348	72.81
XXV	c;e	12.3	7.528	61.35
XXVI	b;f	11.2	13.39	172.6
XXVII	b;f	10.6	13.21	181.6
XXVIII	b;f	12.7	14.92	188.8
XXIX	b;f	14.8	16.99	190.6
XXX	b;f	16.6	20.22	218.4
XXXI	b;f	19.3	19.42	203.1
XXXII	b;f	20.2	23.64	249.0

where:

$$a = 0.50M \text{ Cl}^-$$

$$b = 0.40M \text{ Cl}^-$$

$$c = 0.05M \text{ Cl}^-$$

$$d = 4.35 \times 10^{-4}M$$

$$e = 4.60 \times 10^{-4}M$$

$$f = 4.45 \times 10^{-4}M$$

TABLE III

VALUES OF k'_s AND k'_f OBTAINED FROM ARRHENIUS PLOT

<u>Solvent</u>	<u>k'_s (sec⁻¹)</u>			<u>E_a (kcal/mole)</u>
	<u>10°C</u>	<u>15°C</u>	<u>20°C</u>	
0.50M Cl ⁻	15.88	20.32	25.78	8.00
0.40M Cl ⁻	12.79	17.02	22.43	9.26
0.05M Cl ⁻	5.86	10.12	17.25	17.8

<u>Solvent</u>	<u>k'_f (sec⁻¹)</u>			<u>E_a (kcal/mole)</u>
	<u>10°C</u>	<u>15°C</u>	<u>20°C</u>	
0.50M Cl ⁻	180.1	217.1	260.1	6.07
0.40M Cl ⁻	172.3	199.1	229.0	4.70
0.05M Cl ⁻	42.53	87.03	173.8	23.2

FIGURE 1

$\ln K_s$ VS $1/T$
[.50 M CHLORIDE]

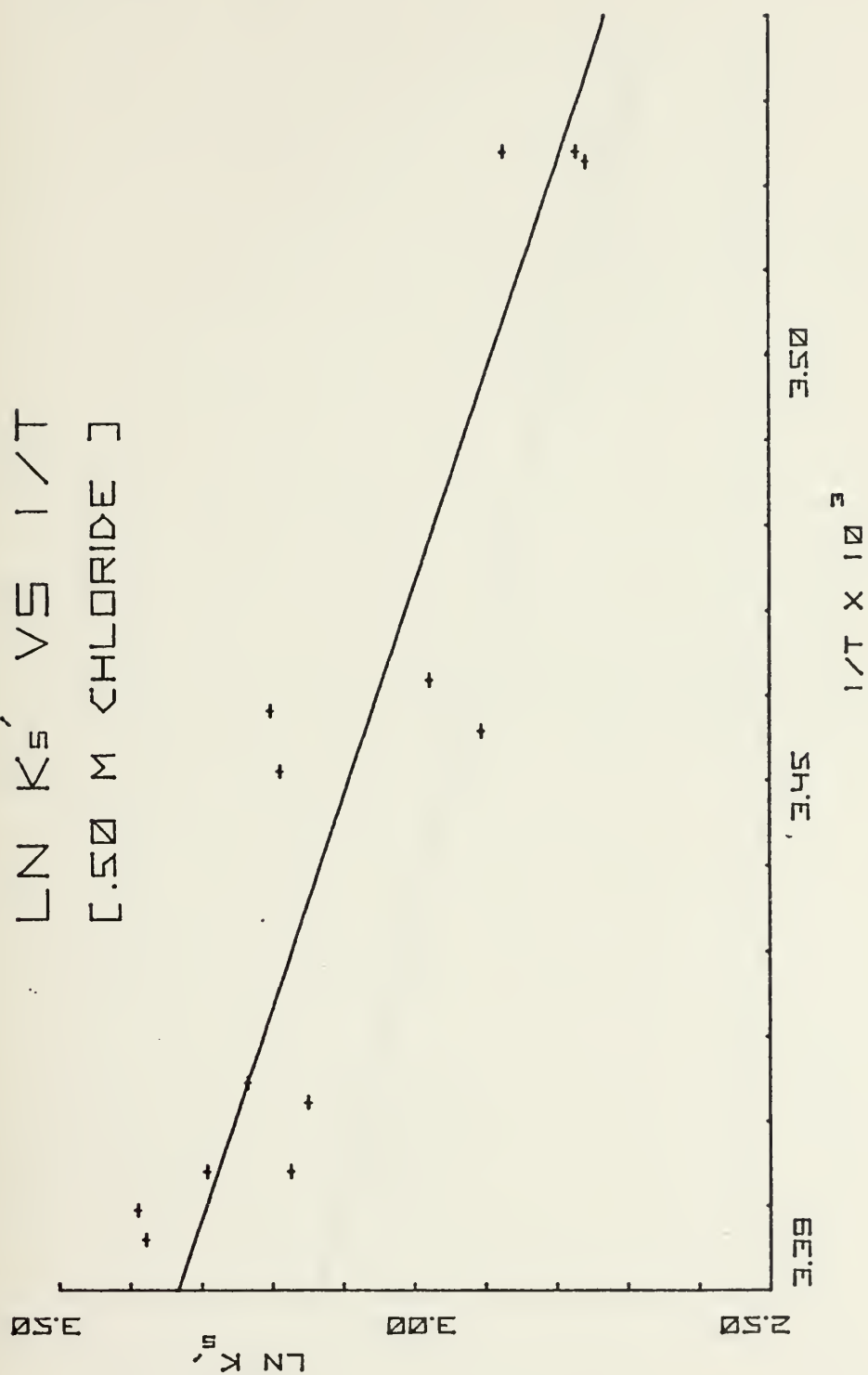
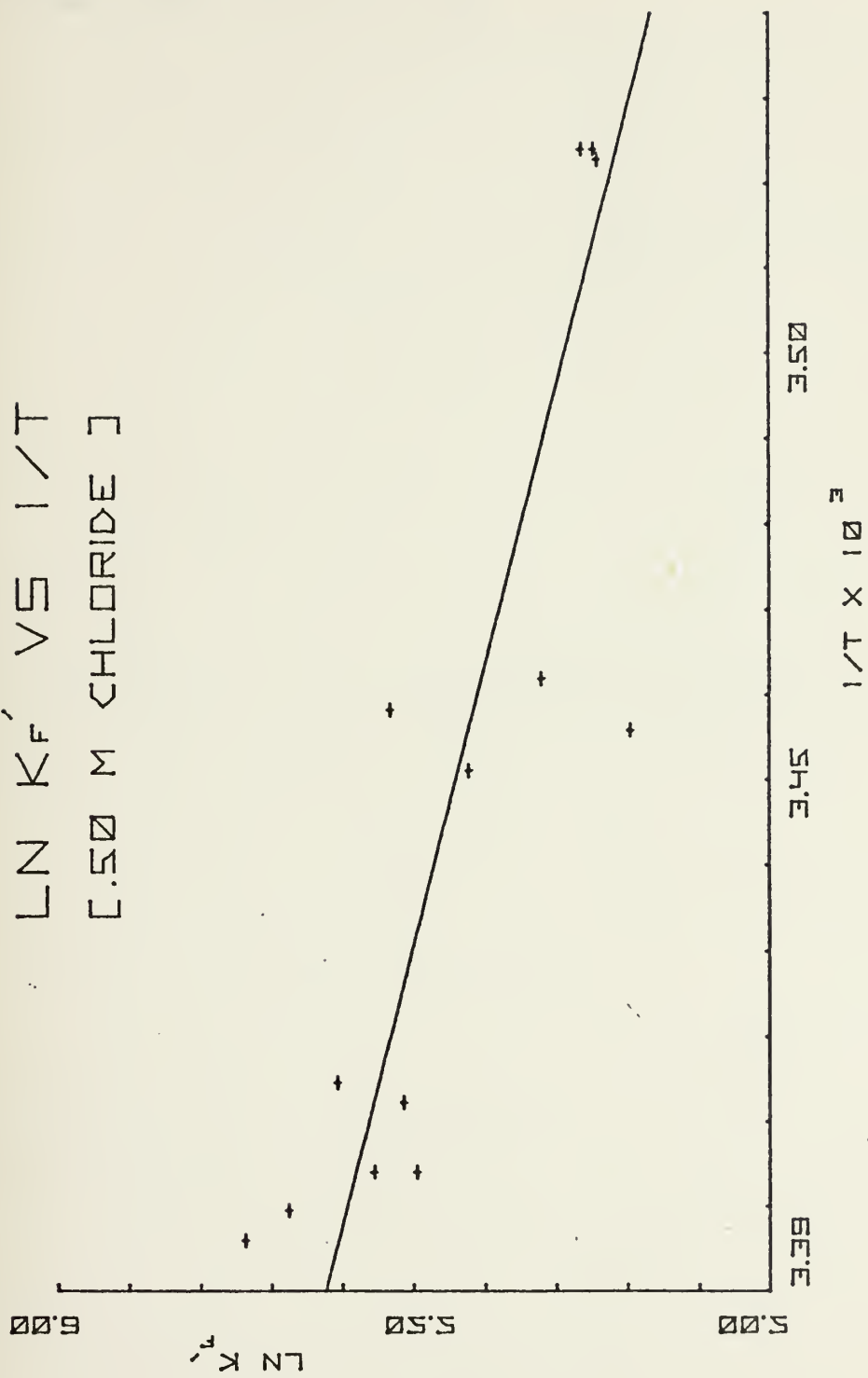


FIGURE 2

LN K_F' VS $1/T$
[.50 M CHLORIDE]



D. ACTIVATION PARAMETERS

The Arrhenius energy of activation E_a was evaluated directly from the plot of $\ln k'$ vs the reciprocal of the absolute temperature, since the slope of this plot equals $-E_a/R$.



IV. DISCUSSION

A. GENERAL

Throughout this research, the data obtained for individual kinetic runs were remarkably consistent. The internal agreement was such that in all but a few runs the choice of straight lines to fit the plotted data points was readily made. Although the pseudo-first order rate constants k'_s and k'_f obtained from the various runs at a fixed chloride concentration did not show the same high degree of consistency, the Arrhenius plots using those data were not difficult to fit, as shown in Figures 1 and 2. The activation energies derived from these were quite reasonable as well (Table III). The specific first and second-order rate constants k_1 and k_2 , for both the fast and slow steps, were anomalous in their behavior. For example, Table IV shows that regardless of which two chloride concentrations were compared, at least one constant decreases with increasing temperature, indicating a negative enthalpy of activation. Other constants show virtually no temperature effect and several show temperature effects that are unreasonably large (a ΔH^\ddagger of about 40 Kcal/mole in one case).

Due to the equivocal nature of these specific constants, it was considered more useful to make comparisons with previously reported values of k'_s and k'_f , the observed pseudo-first order rate constants at a specific chloride concentration, since their behavior seemed reasonable. The constants used were those of the 0.50 M chloride reaction because the largest number of runs had been made at that concentration, and the values used were obtained by extrapolating the data to 25°C. The values

TABLE IV

VALUES OF SPECIFIC FIRST- AND SECOND-ORDER RATE CONSTANTS

 k_1 units are sec^{-1} ; k_2 units are $\text{m}^{-1}\text{sec}^{-1}$

<u>Plots Compared</u>	<u>Constant</u>	<u>10°C</u>	<u>15°C</u>	<u>20°C</u>
0.50M Cl^- and 0.40M Cl^-	k_{1s}	.4636	3.842	9.013
	k_{2s}	30.83	32.85	33.54
	k_{1f}	141.2	127.3	104.7
	k_{2f}	77.64	179.7	310.8
0.40M Cl^- and 0.05M Cl^-	k_{1s}	4.871	9.168	16.51
	k_{2s}	19.81	19.64	14.81
	k_{1f}	23.99	71.01	165.9
	k_{2f}	370.7	320.3	157.9
0.50M Cl^- and 0.05M Cl^-	k_{1s}	4.749	9.021	16.30
	k_{2s}	22.25	22.60	18.97
	k_{1f}	27.25	72.58	164.2
	k_{2f}	305.6	289.1	191.9

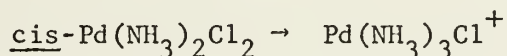
obtained in this manner were $k'_s = 32.5 \text{ sec}^{-1}$ and $k'_f = 310 \text{ sec}^{-1}$.

B. COMPARISON WITH PREVIOUS DATA

1. Assignment of fast and slow steps

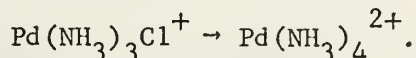
Table V is a compilation of existing data pertinent to the various parts of the reaction studied by this author. Most k' values listed in this table were obtained by adjusting the reported constants the condition of .50 M chloride.

Midas (Ref. 7) made the arbitrary assignment that the slow step of the reaction sequence was the first step, namely:



and that the fast step was the second. Actually, there is no direct evidence as to which step is which, and direct assignment cannot be made from his data, due to the problem of reversibility. Likewise, it cannot be made from the data of the present research since accurate ϵ values are not known for $\text{Pd(NH}_3)_3\text{Cl}^+$ or $\text{Pd(NH}_3)_4^{2+}$ in the charge-transfer region.

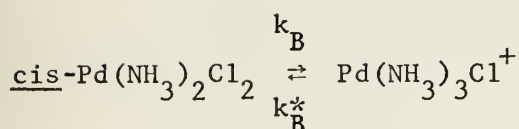
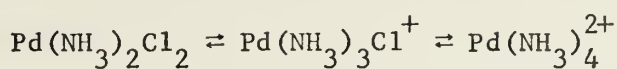
The data which can be reliably used as a starting point are those calculated for k' (from the data of Reinhardt and Sparkes [Ref. 4]) shown in Table V for the reaction step



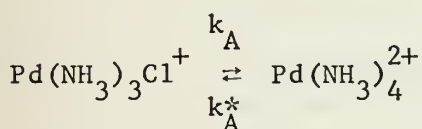
The fact that the present value of k'_f shows general agreement with these values is considered good evidence that this is the fast step. Having made this association, Midas' choice of fast and slow steps can now be supported by the agreement of his k' values with those of this report. As previously discussed, Reinhardt and Monk (Ref. 6) had estimated that

TABLE V

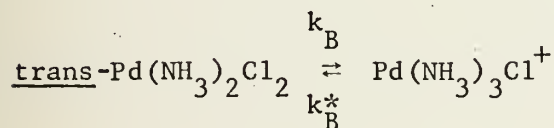
A COMPILATION OF DATA FOR THE REACTIONS



Conditions	$k_{B1}(\text{sec}^{-1})$	$k_{B2}(\text{M}^{-1}\text{sec}^{-1})$	$k'(\text{sec}^{-1})^a$	K_{eq}
$T = 25^\circ\text{C}$				
$\mu = 1.0\text{M}$	13.2 ^b	12 ^b	19.2 ^c	--
$\mu = 0.8\text{M}$	8.9 ^d	5.1 ^d	11.45 ^c	--
$\mu = 1.0\text{M}$	---	---	32.46 ^e	--



Conditions	$k_{A1}(\text{sec}^{-1})$	$k_{A2}(\text{sec}^{-1})$	$k'(\text{sec}^{-1})^a$	K_{eq}
$T = 25^\circ\text{C}$				
$\mu = 1.0\text{M}$	18 ^f	116 ^g *0.0071 ⁱ	76 ^c 89.4 ^j 111 ^k	1.64x10 ⁵ h
$\mu = 0.8\text{M}$	135 ^d	64 ^d	167 ^c	--
$\mu = 1.0\text{M}$	---	---	309.8 ^e	--



Conditions	$k_{B1}(\text{sec}^{-1})$	$k_{B2}(\text{sec}^{-1})$	$k'(\text{sec}^{-1})$	K_{eq}
$T = 25^\circ\text{C}$				
$\mu = 1.0\text{M}$	*9x10 ⁻⁴ i	* 0.030 ⁱ	*0.016 ^c *0.0225 ^l	1.64x10 ⁵ h
		1800 ^{g,m}	1000 ^g	

NOTE 1: * values refer to the reverse rate step constants

Note 2: a) k' values have been computed for the condition of 0.50M Cl^- except where otherwise noted (k and j).

b) Ref. 6

c) Calculated from component first- and second-order rate constants.

d) Ref. 7

e) Extrapolated values from this research.

f) Computed from aquation rate constant, Refs. 4, 11 and K_{eq} .

g) Computed from K_{eq} and reverse rate constant.

h) Ref. 3

i) Ref. 4

j) Calculated from K_{eq} using k' values for 0.46M Cl^- reported in Ref. 4

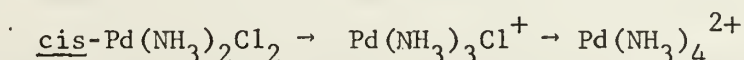
k) Calculated from K_{eq} using k' values for 0.60M Cl^- reported in Ref. 4

l) Reported value for k' for 0.60M Cl^- Ref. 4

m) Assumes trans- $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ predominates over cis-isomer at equilibrium, Ref. 4.

the slower step observed in their study of the ammonation of PdCl_4^{2-} was the step $\text{cis-Pd}(\text{NH}_3)_2\text{Cl}_2 \rightarrow \text{Pd}(\text{NH}_3)_3\text{Cl}^+$. Based on the available data and the arguments presented above, it seems reasonable to say that their assignment of the data to this reaction step was correct.

To summarize, then: the slow step of the reaction appears to be the first step and the fast, the second, for the sequence



C. CIS-TRANS ISOMERIZATION IN $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$

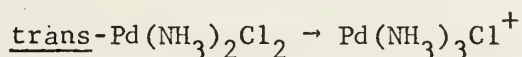
In his review of replacement reactions in square planar complexes, Cattalini (Ref. 19) points out that study of isomerizations has been confined largely to equilibrium studies and photochemical reactions. The isomerization in solution of cis- and trans-geometrical isomers of this type is known to be catalyzed by the presence of free ligand (Ref. 19).

The present author feels that some of the anomalies in his data may very well stem from isomerization of the cis- $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ complex. Some limited studies along these lines were made early in this investigation to try to determine how long a solution of 1.0×10^{-4} formal cis complex in 1.0 M sodium chloride could be stored without showing signs of isomerization. Poë and Vaughan (Ref. 5) had shown that cis- $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ reacts with chloride roughly 100 times faster than the trans-complex. By studying the reaction of solutions of cis-isomer with hydrochloric acid spectrophotometrically, it was thought that a change in rate of reaction with aging of the solution could be correlated with isomerization.

By this criterion, solutions of cis- $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ in 1.0 M chloride appeared to remain stable for weeks if care was taken initially to remove

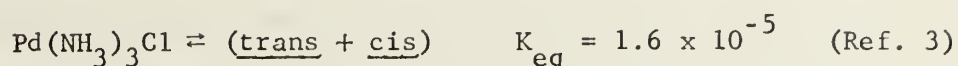
carbon dioxide from the solvent before dissolving the palladium compound. Interpretation of the data was difficult for two reasons. First, both the stock trans-compound and a portion of the stock that had been carefully repurified by the method of Reinhardt, et al (Ref. 3) showed a rapid initial reaction rate. This indicated that even in a solution of the repurified sample, there was at least a small percentage of cis-isomer present. Second, there is a possibility that isomerization equilibrium could have occurred even before the solution of cis-complex has reacted, thus giving the apparent stability with aging. Time was not available to permit pursuing the point further, but it would be a valuable field for future research. Isomerization of this nature should be well suited for study by rapid kinetics techniques.

Earlier in this report (see Introduction) the author discussed the assumption made by Reinhardt and Sparkes (Ref. 4) that the reaction of $\text{Pd}(\text{NH}_3)_3\text{Cl}^+$ with chloride led largely to the production of the trans-isomer of $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ as would be predicted from the greater "trans directing influence" (Ref. 19) of the chloride ligand in $\text{Pd}(\text{NH}_3)_3\text{Cl}^+$. From their data, a calculated k' of 1000 sec^{-1} was obtained for the reaction



If a value close to this had been obtained from studying the corresponding step for the cis-isomer, the assumption made in Ref. 4 would be suspect. As it is, the k' of 32.46 sec^{-1} calculated in this study was sufficiently different from their k' to support their assumption well. It certainly means that, at least, a substantial amount of trans-complex is formed. If there is, moreover, an appreciable equilibrium concentration of both cis and trans forms, then one can make a rough

estimate of the rate of formation of cis from $\text{Pd}(\text{NH}_3)_3\text{Cl}^+$. For



$$\text{i.e.} \quad \frac{[(\text{trans}) + (\text{cis})](\text{NH}_3)}{(\text{Cl}^-)[\text{Pd}(\text{NH}_3)_3\text{Cl}^+]} = K_{\text{eq}}$$

and if (cis) is approximately equal to (trans) then the equilibrium constant for each species individually is roughly 1×10^{-5} because

$$K_{\text{eq}} = k_{\text{eq}} \frac{\text{cis}}{(\text{Cl}^-)[\text{Pd}(\text{NH}_3)_3\text{Cl}^+]} + K_{\text{eq}} \frac{\text{trans}}{(\text{Cl}^-)[\text{Pd}(\text{NH}_3)_3\text{Cl}^+]}$$

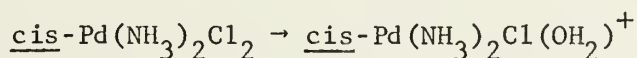
Using the value for k' obtained in this research for the conversion of cis- $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ to $\text{Pd}(\text{NH}_3)_3\text{Cl}^+$ and the rough equilibrium value above, a simple calculation produces an estimated k' of 0.0003 sec^{-1} for the formation of the cis-isomer from $\text{Pd}(\text{NH}_3)_3\text{Cl}^+$. Comparing this with values in Table V for the similar formation of trans-isomer from $\text{Pd}(\text{NH}_3)_3\text{Cl}^+$ ($k' \sim 0.02 \text{ sec}^{-1}$) one can again argue that the trans- $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ is preferred kinetically by a large ratio.

D. OTHER CONSIDERATIONS

In retrospect, there are a few small observations which may give some additional insight into the source of the irregular behavior shown by the data. For example, in several cases where a sequence of kinetic runs was made using the same stock solution, the initial value of the absorbance of the sample solution prior to mixing increased somewhat with successive runs while the values of D_∞ showed only normal experimental fluctuations. The extent of rinsing and preparing of the sample cell was such that it is not felt that contamination was responsible. There is always the possibility that drift in the instrument was the

cause, but considering the lengthy warm-up periods allowed, it seems more likely that actual changes in the nature of the solution were the source of this phenomena. Since accurate values of the molar extinction coefficients of both cis and trans isomers are not available, isomerization to the trans complex might well be taking place.

A second observation of a similar nature came about while studying the solutions of palladium complex containing lower chloride concentrations. As they were made up, these solutions were 1.00×10^{-4} formal in complex and 0.30 M and 0.10 M in sodium chloride. The ionic strength was brought up to unity by addition of sodium perchlorate but this was not necessary for the solutions of complex in 1.0 M chloride. Whereas the initial absorbance values for the unmixed solutions in 1.0 M chloride were generally about 0.7 to 0.8 absorbance units, those of the lower chloride solutions at the same wavelength (235 nm) were about 0.55 to 0.65. If this was not due to aquation



or to calibration and tuning given the instrument in the time after the high-chloride runs had been completed (which is doubtful), it could be speculated that possible impurities in the sodium perchlorate reacted with the dissolved complex.

At these lower chloride concentrations, a sequence of runs from the same solution again showed the general drift in initial absorbance values that might indicate isomerization to trans-Pd(NH₃)₂Cl₂.

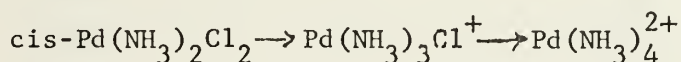
There remains the possibility also, that under the conditions utilized in this research, the studied reaction does not have a simple inverse first-order rate dependence upon the concentration of chloride.

Extensive effort might be required to resolve this question. However, it should be examined if studies of the most probable cause of the anomalies in the present results, namely, cis-trans isomerization, do not provide the hoped-for explanation.

APPENDIX A

ABSORBANCE DATA FOR INDIVIDUAL KINETIC RUNS

This appendix contains all absorbance vs. time data from the kinetic runs used in this research. Runs XI - XIII were not used in this research due to faulty thermocouple behavior and thus are not included. All times are in seconds. The constants k_s and k_f are the observed pseudo-first-order rate constants for the slow and fast steps respectively, of the following reaction;



In all runs the concentration of the $\text{cis-Pd}(\text{NH}_3)_2\text{Cl}_2$ complex is 5×10^{-5} formal.

RUN I

$T = 19.6^\circ\text{C}$ $(\text{Cl}^-) = 0.50\text{M}$ $(\text{NH}_3) = 4.85 \times 10^{-4}\text{M}$ $k_s = 0.0221 \text{ sec}^{-1}$
 $k_f = 0.237 \text{ sec}^{-1}$ $D_\infty = 0.032$

<u>Time</u>	<u>Absorbance</u>	$\lambda = 235$	<u>Time</u>	<u>Absorbance</u>
3	0.212		29	0.084
5	0.175		33	0.080
7	0.152		37	0.076
9	0.136		41	0.073
11	0.122		45	0.069
13	0.114		49	0.067
15	0.110		53	0.064
17	0.105		57	0.061
21	0.098		61	0.060
23	0.093		65	0.058
25	0.089		69	0.056

RUN II

$T = 20.6^{\circ}\text{C}$ $(\text{Cl}^{-}) = 0.50\text{M}$ $(\text{NH}_3) = 4.85 \times 10^{-4}\text{M}$ $k_s = 0.0221 \text{ sec}^{-1}$
 $k_f = 0.225 \text{ sec}^{-1}$ $D_{\infty} = 0.029$

<u>Time</u>	<u>Absorbance</u>	$\lambda = 235$	<u>Time</u>	<u>Absorbance</u>
9	0.159		41	0.073
11	0.140		45	0.071
13	0.127		49	0.068
15	0.119		53	0.066
17	0.111		57	0.063
19	0.106		61	0.061
21	0.101		65	0.058
23	0.098		69	0.055
25	0.096		73	0.053
29	0.088		77	0.052
33	0.082		81	0.049
37	0.078			

RUN III

$T = 20.6^{\circ}\text{C}$ $(\text{Cl}^{-}) = 0.50\text{M}$ $(\text{NH}_3) = 4.85 \times 10^{-4}\text{M}$ $k_s = 0.0234 \text{ sec}^{-1}$
 $k_f = 0.0212 \text{ sec}^{-1}$ $D_{\infty} = 0.029$

<u>Time</u>	<u>Absorbance</u>	$\lambda = 235$	<u>Time</u>	<u>Absorbance</u>
4	0.220		32	0.081
6	0.184		36	0.077
8	0.160		40	0.072
10	0.152		44	0.068
12	0.129		48	0.065
14	0.122		52	0.062
16	0.113		56	0.059
18	0.108		60	0.058
20	0.101		64	0.055
22	0.098		68	0.053
24	0.093		72	0.051
28	0.087		76	0.049

RUN IV

$T = 19.9^{\circ}\text{C}$ $(\text{Cl}^{-}) = 0.50\text{M}$ $(\text{NH}_3) = 4.85 \times 10^{-4}\text{M}$ $k_s = 0.0213 \text{ sec}^{-1}$
 $k_f = 0.216 \text{ sec}^{-1}$ $D_{\infty} = 0.025$

<u>Time</u>	<u>Absorbance</u>	$\lambda = 235$	<u>Time</u>	<u>Absorbance</u>
3	0.221		29	0.079
5	0.169		33	0.075
7	0.151		37	0.071
9	0.132		41	0.068
11	0.118		45	0.062
13	0.110		49	0.059
15	0.104		53	0.058
17	0.100		61	0.053
19	0.095		65	0.051
21	0.090		69	0.048
23	0.085		73	0.045
25	0.082			

RUN V

$T = 21.0^{\circ}\text{C}$ $(\text{Cl}^{-}) = 0.50\text{M}$ $(\text{NH}_3) = 4.85 \times 10^{-4}\text{M}$ $k_s = 0.0258 \text{ sec}^{-1}$
 $k_f = 0.254 \text{ sec}^{-1}$ $D_{\infty} = 0.035$

<u>Time</u>	<u>Absorbance</u>	$\lambda = 235$	<u>Time</u>	<u>Absorbance</u>
3	0.226		29	0.085
5	0.180		33	0.078
7	0.155		37	0.075
9	0.140		41	0.071
11	0.127		45	0.068
13	0.119		49	0.064
15	0.111		53	0.062
17	0.105		57	0.059
19	0.101		61	0.057
21	0.097		65	0.055
23	0.093		69	0.053
25	0.090			

RUN VI

$$T = 21.3^{\circ}\text{C} \quad (\text{Cl}^{-} = 0.50\text{M} \quad (\text{NH}_3) = 4.85 \times 10^{-4}\text{M} \quad k_s = 0.0255 \text{ sec}^{-1}$$

$$k_f = 0.270 \text{ sec}^{-1} \quad D_{\infty} = 0.029$$

<u>Time</u>	<u>Absorbance</u>	$\lambda = 235$	<u>Time</u>	<u>Absorbance</u>
2	0.274		28	0.086
4	0.216		30	0.083
6	0.180		34	0.079
8	0.157		38	0.075
10	0.141		42	0.071
12	0.129		46	0.068
14	0.120		50	0.066
16	0.112		54	0.063
18	0.107		58	0.061
20	0.102		62	0.058
22	0.098		66	0.055
24	0.095		70	0.053
26	0.090			

RUN VII

$$T = 15.7^{\circ}\text{C} \quad (\text{Cl}^{-}) = 0.50\text{M} \quad (\text{NH}_3) = 4.85 \times 10^{-4} \quad k_s = 0.0171 \text{ sec}^{-1}$$

$$k_f = 0.178 \text{ sec}^{-1} \quad D_{\infty} = 0.00$$

<u>Time</u>	<u>Absorbance</u>	$\lambda = 235$	<u>Time</u>	<u>Absorbance</u>
1	0.262		25	0.062
3	0.187		29	0.057
5	0.151		33	0.052
7	0.128		37	0.048
9	0.112		41	0.044
11	0.100		45	0.042
13	0.092		49	0.040
15	0.083		53	0.037
17	0.076		57	0.034
19	0.073		61	0.033
21	0.069		65	0.031
23	0.065		73	0.027

RUN VIII

T = 16.6° C (Cl⁻) = 0.50M (NH₃) = 4.85x10⁻⁴M k_s = 0.0211 sec⁻¹
 k_f = 0.197 sec⁻¹ D_∞ = 0.00

<u>Time</u>	<u>Absorbance</u>	λ = 235	<u>Time</u>	<u>Absorbance</u>
3	0.206		29	0.051
5	0.164		33	0.047
7	0.133		37	0.043
9	0.112		41	0.040
11	0.099		45	0.037
13	0.086		49	0.033
15	0.077		53	0.031
17	0.070		57	0.028
19	0.064		61	0.026
21	0.061		65	0.024
23	0.058		69	0.022
25	0.055		73	0.021

RUN IX

T = 16.0° C (Cl⁻) = 0.50M (NH₃) = 4.85x10⁻⁴ k_s = 0.0214 sec⁻¹
 k_f = 0.220 sec⁻¹ D_∞ = 0.011

<u>Time</u>	<u>Absorbance</u>	λ = 235	<u>Time</u>	<u>Absorbance</u>
2	0.300		30	0.058
4	0.195		34	0.053
6	0.155		38	0.050
8	0.127		42	0.047
10	0.110		46	0.044
12	0.099		50	0.042
14	0.088		54	0.039
16	0.081		58	0.037
18	0.075		62	0.034
20	0.072		66	0.032
22	0.068		70	0.031
24	0.065		74	0.029
26	0.062			

RUN X

$T = 16.2^{\circ}\text{C}$ $(\text{Cl}^{-}) = 0.50\text{M}$ $(\text{NH}_3) = 4.85 \times 10^{-4}$ $k_s = 0.0159 \text{ sec}^{-1}$
 $k_f = 0.157 \text{ sec}^{-1}$ $D_{\infty} = 0.002$

<u>Time</u>	<u>Absorbance</u>	$\lambda = 235$	<u>Time</u>	<u>Absorbance</u>
2	0.236		30	0.058
4	0.178		34	0.053
6	0.147		38	0.050
8	0.128		42	0.047
10	0.111		46	0.044
12	0.100		50	0.041
14	0.090		54	0.039
16	0.084		58	0.037
18	0.078		62	0.035
20	0.073		66	0.032
22	0.069		70	0.031
24	0.066		74	0.029
26	0.063			

RUN XIV

$T = 10.7^{\circ}\text{C}$ $(\text{Cl}^{-}) = 0.50\text{M}$ $(\text{NH}_3) = 5.10 \times 10^{-4}\text{M}$ $k_s = 0.0145 \text{ sec}^{-1}$
 $k_f = 0.174 \text{ sec}^{-1}$ $D_{\infty} = 0.025$

<u>Time</u>	<u>Absorbance</u>	$\lambda = 235$	<u>Time</u>	<u>Absorbance</u>
4	0.237		28	0.092
6	0.195		32	0.087
8	0.171		36	0.083
10	0.153		40	0.079
12	0.137		44	0.076
14	0.126		48	0.073
16	0.117		52	0.071
18	0.111		56	0.069
20	0.105		60	0.066
22	0.102		64	0.064
24	0.098		68	0.062
26	0.095		72	0.060

RUN XV

$$T = 10.6^{\circ}C \quad (Cl^{-}) = 0.50M \quad (NH_3) = 5.10 \times 10^{-4}M \quad k_s = 0.0163 \text{ sec}^{-1}$$

$$k_f = 0.175 \text{ sec}^{-1} \quad D_{\infty} = 0.048$$

<u>Time</u>	<u>Absorbance</u>	$\lambda = 235$	<u>Time</u>	<u>Absorbance</u>
3	0.289		27	0.115
5	0.243		31	0.109
7	0.211		35	0.106
9	0.187		39	0.103
11	0.172		43	0.099
13	0.157		47	0.095
15	0.146		51	0.093
17	0.138		55	0.090
19	0.131		59	0.088
21	0.127		63	0.084
23	0.122		67	0.083
25	0.118		71	0.081

RUN XVI

$$T = 10.6^{\circ}C \quad (Cl^{-}) = 0.50M \quad (NH_3) = 5.10 \times 10^{-4}M \quad k_s = 0.0147 \text{ sec}^{-1}$$

$$k_f = 0.178 \text{ sec}^{-1} \quad D_{\infty} = 0.030$$

<u>Time</u>	<u>Absorbance</u>	$\lambda = 235$	<u>Time</u>	<u>Absorbance</u>
2	0.311		32	0.096
4	0.248		34	0.094
6	0.210		38	0.090
8	0.183		42	0.088
16	0.133		46	0.083
18	0.122		50	0.080
20	0.116		54	0.078
22	0.111		58	0.075
24	0.108		62	0.073
26	0.106		66	0.072
28	0.102		70	0.069
30	0.099			

RUN XVII

$T = 10.3^{\circ}\text{C}$ $(\text{Cl}^-) = 0.05\text{M}$ $(\text{NH}_3) = 5.10 \times 10^{-4}\text{M}$ $k_s = 0.0531 \text{ sec}^{-1}$
 $k_f = 0.382 \text{ sec}^{-1}$ $D_{\infty} = 0.022$

<u>Time</u>	<u>Absorbance</u>	$\lambda = 235$	<u>Time</u>	<u>Absorbance</u>
2	0.232		18	0.058
3	0.179		20	0.054
4	0.151		22	0.051
5	0.131		24	0.048
6	0.113		26	0.045
7	0.103		28	0.043
8	0.095		30	0.041
10	0.083		32	0.040
12	0.074		34	0.038
14	0.068		38	0.035
16	0.063		42	0.032

RUN XVIII

$T = 10.3^{\circ}\text{C}$ $(\text{Cl}^-) = 0.05\text{M}$ $(\text{NH}_3) = 5.10 \times 10^{-4}\text{M}$ $k_s = 0.0555 \text{ sec}^{-1}$
 $k_f = 0.394 \text{ sec}^{-1}$ $D_{\infty} = 0.021$

<u>Time</u>	<u>Absorbance</u>	$\lambda = 235$	<u>Time</u>	<u>Absorbance</u>
2	0.216		18	0.055
3	0.169		20	0.052
4	0.145		22	0.049
5	0.124		24	0.046
6	0.108		26	0.043
7	0.098		28	0.041
8	0.089		30	0.039
10	0.080		32	0.037
12	0.072		34	0.036
14	0.064		38	0.032
16	0.059			

RUN XIX

$T = 10.3^{\circ}\text{C}$ $(\text{Cl}^{-}) = 0.05\text{M}$ $(\text{NH}_3) = 5.10 \times 10^{-3}\text{M}$ $k_s = 0.0594 \text{ sec}^{-1}$
 $k_f = 0.05 \text{ sec}^{-1}$ $D_{\infty} = 0.017$

<u>Time</u>	<u>Absorbance</u>	$\lambda = 235$	<u>Time</u>	<u>Absorbance</u>
2	0.181		16	0.053
3	0.142		18	0.049
4	0.121		20	0.045
5	0.107		22	0.042
6	0.097		24	0.039
7	0.088		26	0.037
8	0.082		28	0.035
10	0.072		30	0.033
12	0.064		34	0.031
14	0.059		38	0.028

RUN XX

$T = 10.3^{\circ}\text{C}$ $(\text{Cl}^{-}) = 0.05\text{M}$ $(\text{NH}_3) = 5.10 \times 10^{-4}\text{M}$ $k_s = 0.0552 \text{ sec}^{-1}$
 $k_f = 0.460 \text{ sec}^{-1}$ $D_{\infty} = 0.017$

<u>Time</u>	<u>Absorbance</u>	$\lambda = 235$	<u>Time</u>	<u>Absorbance</u>
1	0.260		17	0.054
2	0.192		19	0.050
3	0.153		21	0.047
4	0.128		23	0.043
5	0.111		25	0.041
6	0.099		27	0.038
7	0.090		29	0.036
9	0.078		31	0.034
11	0.069		33	0.032
13	0.063		35	0.031
15	0.059		39	0.028

$$T = 14.6^{\circ}\text{C} \quad (\text{Cl}^-) = 0.05\text{M} \quad (\text{NH}_3) = 5.10 \times 10^{-4}\text{M} \quad k_s = 0.0829 \text{ sec}^{-1}$$

$$k_f = 0.708 \text{ sec}^{-1} \quad D_{\infty} = 0.038$$

<u>Time</u>	<u>Absorbance</u>	$\lambda = 235$	<u>Time</u>	<u>Absorbance</u>
2	0.172		12	0.079
3	0.148		13	0.077
4	0.130		14	0.074
5	0.118		16	0.068
6	0.109		18	0.064
7	0.101		20	0.059
8	0.096		22	0.056
9	0.091		24	0.053
10	0.087		26	0.051
11	0.082			

$$T = 14.5^{\circ}\text{C} \quad (\text{Cl}^-) = 0.05\text{M} \quad (\text{NH}_3) = 5.10 \times 10^{-4}\text{M} \quad k_s = 0.0970 \text{ sec}^{-1}$$

$$k_f = 0.819 \text{ sec}^{-1} \quad D_{\infty} = 0.042$$

<u>Time</u>	<u>Absorbance</u>	$\lambda = 235$	<u>Time</u>	<u>Absorbance</u>
2	0.191		11	0.081
3	0.150		12	0.077
4	0.128		13	0.074
5	0.117		14	0.071
6	0.107		16	0.067
7	0.099		18	0.062
8	0.094		20	0.058
9	0.089		22	0.055
10	0.084		24	0.053

RUN XXIII

$T = 14.6^{\circ}\text{C}$ $(\text{Cl}^{-}) = 0.05\text{M}$ $(\text{NH}_3) = 4.95 \times 10^{-4}\text{M}$ $k_s = 0.0882 \text{ sec}^{-1}$
 $k_f = 0.739 \text{ sec}^{-1}$ $D_{\infty} = 0.030$

<u>Time</u>	<u>Absorbance</u>	$\lambda = 235$	<u>Time</u>	<u>Absorbance</u>
2	0.182		12	0.070
3	0.145		13	0.067
4	0.124		14	0.063
5	0.110		15	0.061
6	0.100		16	0.057
7	0.093		18	0.053
8	0.087		20	0.049
9	0.081		22	0.047
10	0.076		24	0.044
11	0.073		26	0.042

RUN XXIV

$T = 14.0^{\circ}\text{C}$ $(\text{Cl}^{-}) = 0.05\text{M}$ $(\text{NH}_3) = 4.95 \times 10^{-4}\text{M}$ $k_s = 0.0743 \text{ sec}^{-1}$
 $k_f = 0.648 \text{ sec}^{-1}$ $D_{\infty} = 0.012$

<u>Time</u>	<u>Absorbance</u>	$\lambda = 233$	<u>Time</u>	<u>Absorbance</u>
2	0.188		13	0.055
3	0.145		14	0.052
4	0.120		15	0.049
5	0.103		17	0.044
6	0.095		19	0.039
7	0.085		21	0.036
8	0.079		23	0.033
9	0.073		25	0.030
10	0.068		27	0.028
11	0.064		29	0.026
12	0.059			

RUN XXV

$T = 12.3^{\circ}\text{C}$ $(\text{Cl}^{-}) = 0.05\text{M}$ $(\text{NH}_3) = 4.95 \times 10^{-4}\text{M}$ $k_s = 0.0670 \text{ sec}^{-1}$
 $k_f = 0.546 \text{ sec}^{-1}$ $D_{\infty} = 0.014$

<u>Time</u>	<u>Absorbance</u>	$\lambda = 233$	<u>Time</u>	<u>Absorbance</u>
2	0.198		13	0.062
3	0.151		14	0.058
4	0.127		15	0.056
5	0.112		16	0.053
6	0.099		17	0.050
7	0.091		19	0.045
8	0.084		21	0.042
9	0.078		23	0.039
10	0.073		25	0.035
11	0.069		27	0.033
12	0.065			

RUN XXVI

$T = 11.2^{\circ}\text{C}$ $(\text{Cl}^{-}) = 0.40\text{M}$ $(\text{NH}_3) = 4.95 \times 10^{-4}\text{M}$ $k_s = 0.0149 \text{ sec}^{-1}$
 $k_f = 0.192 \text{ sec}^{-1}$ $D_{\infty} = 0.015$

<u>Time</u>	<u>Absorbance</u>	$\lambda = 232$	<u>Time</u>	<u>Absorbance</u>
3	0.317		26	0.125
4	0.290		28	0.120
6	0.247		32	0.115
8	0.217		36	0.108
10	0.196		40	0.103
12	0.178		44	0.099
14	0.164		48	0.095
16	0.154		52	0.091
18	0.147		56	0.087
20	0.140		60	0.082
22	0.134		64	0.079
24	0.129		68	0.077

RUN XXVII

$T = 10.6^{\circ}\text{C}$ $(\text{Cl}^{-}) = 0.40\text{M}$ $(\text{NH}_3) = 4.95 \times 10^{-4}\text{M}$ $k_s = 0.0147 \text{ sec}^{-1}$
 $k_f = 0.202 \text{ sec}^{-1}$ $D_{\infty} = 0.024$

<u>Time</u>	<u>Absorbance</u>	$\lambda = 232$	<u>Time</u>	<u>Absorbance</u>
3	0.319		28	0.128
4	0.296		30	0.125
6	0.250		34	0.118
8	0.222		38	0.112
10	0.198		42	0.107
12	0.181		46	0.102
14	0.169		50	0.098
16	0.159		54	0.093
18	0.151		58	0.090
20	0.145		62	0.087
22	0.140		66	0.083
24	0.135		70	0.080
26	0.131			

RUN XXVIII

$T = 12.7^{\circ}\text{C}$ $(\text{Cl}^{-}) = 0.40\text{M}$ $(\text{NH}_3) = 4.95 \times 10^{-4}\text{M}$ $k_s = 0.0166 \text{ sec}^{-1}$
 $k_f = 0.210 \text{ sec}^{-1}$ $D_{\infty} = 0.020$

<u>Time</u>	<u>Absorbance</u>	$\lambda = 232$	<u>Time</u>	<u>Absorbance</u>
3	0.320		27	0.118
5	0.252		29	0.115
7	0.215		33	0.109
9	0.197		37	0.102
11	0.175		41	0.098
13	0.163		45	0.093
15	0.152		49	0.089
17	0.142		53	0.084
19	0.137		57	0.080
21	0.132		61	0.077
23	0.128		65	0.073
25	0.122		69	0.070

$$T = 14.8^{\circ}\text{C} \quad (\text{Cl}^-) = 0.40\text{M} \quad (\text{NH}_3) = 4.95 \times 10^{-4}\text{M} \quad k_s = 0.0189 \text{ sec}^{-1}$$

$$k_f = 0.217 \text{ sec}^{-1} \quad D_{\infty} = 0.015$$

<u>Time</u>	<u>Absorbance</u>	$\lambda = 232$	<u>Time</u>	<u>Absorbance</u>
3	0.290		26	0.113
4	0.262		30	0.108
6	0.224		34	0.102
8	0.198		38	0.044
10	0.178		42	0.088
12	0.161		46	0.083
14	0.150		50	0.079
16	0.140		54	0.074
18	0.134		58	0.070
20	0.128		62	0.068
22	0.122		66	0.064
24	0.119		70	0.060

RUN XXX

$$T = 16.6^{\circ}\text{C} \quad (\text{Cl}^{-}) = 0.040\text{M} \quad (\text{NH}_3) = 4.95 \times 10^{-4}\text{M} \quad k_s = 0.0225 \text{ sec}^{-1}$$

$$k_f = 0.243 \text{ sec}^{-1} \quad D_{\infty} = 0.018$$

<u>Time</u>	<u>Absorbance</u>	$\lambda = 232$	<u>Time</u>	<u>Absorbance</u>
3	0.310		24	0.112
4	0.278		26	0.107
5	0.251		30	0.098
6	0.236		34	0.093
7	0.212		38	0.087
8	0.195		42	0.081
10	0.169		46	0.076
12	0.157		50	0.072
14	0.147		54	0.068
16	0.138		58	0.063
18	0.131		62	0.060
20	0.124		66	0.058
22	0.119		70	0.054

$$T = 19.3^{\circ}\text{C} \quad (\text{Cl}^-) = 0.40\text{M} \quad (\text{NH}_3) = 4.95 \times 10^{-4}\text{M} \quad k_s = 0.0216 \text{ sec}^{-1}$$

$$k_f = 0.226 \text{ sec}^{-1} \quad D_{\infty} = 0.013$$

<u>Time</u>	<u>Absorbance</u>	$\lambda = 232$	<u>Time</u>	<u>Absorbance</u>
3	0.314		27	0.108
5	0.256		29	0.103
7	0.219		33	0.097
9	0.191		37	0.089
11	0.168		41	0.083
13	0.155		45	0.078
15	0.143		49	0.072
17	0.134		53	0.069
19	0.128		57	0.063
21	0.122		61	0.059
23	0.117		65	0.056
25	0.112		69	0.053

$$T = 20.2^{\circ}\text{C} \quad (\text{Cl}^-) = 0.40\text{M} \quad (\text{NH}_3) = 4.95 \times 10^{-4}\text{M} \quad k_s = 0.0263 \text{ sec}^{-1}$$

$$k_f = 0.277 \text{ sec}^{-1} \quad D_{\infty} = 0.019$$

<u>Time</u>	<u>Absorbance</u>	$\lambda = 232$	<u>Time</u>	<u>Absorbance</u>
3	0.281		29	0.090
5	0.220		31	0.087
7	0.184		33	0.082
9	0.164		37	0.077
11	0.150		41	0.072
13	0.136		45	0.067
15	0.127		49	0.062
17	0.119		53	0.058
19	0.113		57	0.054
21	0.108		61	0.052
23	0.103		65	0.049
25	0.099		69	0.047
27	0.094			

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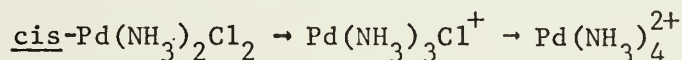
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The reaction of cis-dichlorodiamminepalladium(II) with ammonia:



was studied over the temperature range 10°-21°C using ultraviolet spectroscopy. Three chloride concentrations were utilized in the kinetic runs; 0.50M, 0.40M, and 0.05M, and in all runs $\mu = 1.0\text{M}$.

Slow and fast steps are identified and the observed rate constants for these steps, k'_s and k'_f respectively, were obtained. The following extrapolated values were calculated for 25°C: $k'_s = 32.5 \text{ sec}^{-1}$, and $k'_f = 310 \text{ sec}^{-1}$. Using these values, comparisons are drawn with previously reported data.

Palladium complex kinetics



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